RATE DETERMINING STEPS STUDY IN ACID DYES SORPTION FROM AQUEOUS SOLUTIONS BY ORANGE PEEL

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ABSTRACT

Batch studies of acid dyes sorption by orange peel were carried out to identify the main rate controlling steps in the overall uptake mechanism, using a single external mass transfer diffusion model and intraparticle mass transfer diffusion model. Certain classical parameters influencing dyes sorption mechanisms namely: initial acid dyes concentration and dye type were investigated. The approach chosen in this study was restricted to an interpretation and subsequent identification of mass transfer coefficients by separating the two mechanisms, based on the adequacy of correspondence models with experimental data of these parameters. The process mechanism was found to be complex, consisting of external mass transfer and intraparticle mass transfer diffusion. Analysis of mechanistic steps involved in the sorption process confirms that the sorption process is particle-diffusion-controlled, with some predominance of some external mass transfer at the initial stages for the different experimental parameters studied.

Keywords: Sorption; Acid dyes; Orange peel; External film mass transfer; Intraparticle diffusion

INTRODUCTION

Synthetic dyes are extensively used by industries including dye houses, paper printers, textile dyers, colour photography and as additives in petroleum products (Zollinger [1], Selvam et al. [2]). Over 7×10^5 tons and approximately 10,000 different dyes and pigments are produced annually worldwide, of which about 10% are lost in industrial effluents (Fu and Viraraghavan [3], Robinson et al. [4]). The effluents of these industries are highly coloured and disposal of these wastes into the environment can be extremely deleterious. Their presence in watercourses is aesthetically unacceptable and may be visible at concentration as low as 1 ppm (Zollinger [1]). Moreover, they may also affect photosynthetic activity in aquatic systems by reducing light penetration (O'Mahony et al. [5]). Commercial dyes have a great variety of colors, high stability to light, temperature, detergent and microbial attack. Among the various types of dyes, various acid dyes are used to color nylon, wool, sole in textile industries, paper and leather. This class of dyes is the most problematic, because they tend to pass through

conventional treatment systems unaffected (Poots et al. [6], Willmott et al. [7], Ofomaja and Ho [8]). Due to low biodegradability of dyes, a conventional biological treatment process is not very effective in treating a dye wastewater. It is usually treated by physical and/or chemical methods (Garg et al. [9]). Although these treatment methods are efficient, they are quite expensive and have operational problems (Garg et al. [9], Kapdan et al. [10]). Sorption of coloured components from aqueous solutions has proven to be an alternative way for decolourization, which is evidenced by the effectiveness of sorption for various dye types (Kapdan et al. [10], Porter et al. [11]). The main drawbacks which exist at the present time are the high costs involved in the regeneration of the adsorbent. Also, since activated carbon is the most widely used and most effective adsorbent, its high cost tends to increase the cost of adsorption systems (Garg et al. [9], Kapdan et al. [10]). As a result, there is a search for low-cost sorbents that can serve as viable alternatives to activated carbon. In this context, considerable research has involved materials of biological origin and many forms of biomass have been shown to be effective dye sorbents. Orange peel waste can be an alternative and favourable sorbent material for pollutants such dyes. However, only a limited number of studies on the use of orange peel waste as a sorbent material have been found in the literature (Namasivayam et al. [12], Sivaraj et al. [13], Annadurai et al. [14], Arami et al. [15], Benaïssa [16]). This low-cost material may be particularly suitable for application in small industries and developing countries. Unlike activated carbons, however, thermal regeneration of the peel wastes is not feasible. Thus, the spent adsorbent may be post-treated with other solid wastes such as activated sludge The sorption kinetics of four acid dyes namely: Nylosane blue, Red erionyl, Yellow erionyl and Red nylosane, in single systems from synthetic aqueous solutions by orange peel has been studied (Benaïssa [16, 17]), however, no information are available for their kinetics controlling mechanisms in the literature. These acid dyes were selected for study initially, because they are generally regarded as the most difficult to remove by conventional techniques in our city and dye contaminants in the discharged effluent Determination of the rate limiting steps in sorption is necessary in order to define the rate parameters for design purposes (Sag and Aktay [18]). For solid-liquid sorption process, the solute transfer process was usually characterized by either external mass transfer (boundary layer diffusion) or intraparticle diffusion or both.

As a continuation of our work (Benaïssa [16, 17]), the aim of this study is to investigate the kinetics controlling mechanisms of acid dyes sorption by orange peel in batch conditions: external mass transfer and intraparticle diffusion. External and intraparticle diffusion models were separately examined according to some sorption parameters such as: initial acid dyes concentration and dye type. The approach chosen in this study was restricted to an interpretation and subsequent identification of mass transfer coefficients, based on the adequacy of correspondence models with experimental data of these parameters.

TRANSFER DIFFUSION MODELS

The sorption of solute on solid particles has been extensively studied. It is generally agreed that there are four consecutive steps which describe the overall sorption process of sorption from a solution by a sorbent particle (Furusawa and Smith [19]). These steps, as adapted to apply to the sorption of dyes by a sorbent particle, are as follows:

1- External mass transfer of dye from the solution bulk to the boundary film;
2- Dye transport from the boundary film to the surface of the sorbent particle;
3- Diffusion of dye within the sorbent particle to the sorption sites: internal diffusion of dye;
4- Final uptake of dye at the sorption sites, which is generally fast.

The first and the second step are external mass transfer resistance steps, depending on various parameters such as agitation and homogeneity of solution. In this study, the agitation given to the solution (400 rpm) is considered as sufficient (Benaïssa [16, 17]) to avoid steps 1 and 2 being controlling steps. In a well – agitated batch system, the boundary layer surrounding the particle is much reduced, reducing the external mass transfer coefficient; hence, the third intraparticle diffusion resistance step is more likely to be the rate controlling step (Sag and Aktay [18]). In the process of establishing the rate limiting step, the fourth step is assumed to be very rapid and is therefore not considered in any kinetic analysis (Findon et al. [20]): sorption is a quasi-instantaneous process, as well as complexation mechanism, precipitation seems to occur with a lower rate (Tsezos and Volesky [21]). The sorption rate will be controlled by the rate of diffusion (Peniche-Covas et al. [22]). Consequently, the two rate limiting steps investigated are external film mass transfer and intraparticle diffusion, either singly or in combination. Models were established to determine the two coefficients initially based on single resistance mass transport analysis (McKay et al. [23]).

1- External mass transfer resistance model

This model assumes that the surface concentration of solute, C_s, on the sorbent is negligible at t = 0, and that intraparticle diffusion is also negligible; it is applied to calculate the initial rate of metal sorption (McKay and Poots [24]). The initial rate of sorption can be determined using the classic mass transfer equation (1) which describes the evolution of metal ion concentration C_t in solution:

$$dC_t / dt = - \beta_L S (C_t - C_s) \tag{1}$$

where β_L is the external mass transfer coefficient, C_t the liquid phase solid concentration at a time t, C_s the liquid phase solute concentration at the particle surface and S the specific surface area for mass transfer.

This equation can be simplified, by substituting the following boundary conditions: $C_t \rightarrow C_o$ and $C_s \rightarrow 0$ when $t \rightarrow 0$; C_o = initial metal ion concentration (McKay et al. [23], McKay and Poots [24], Weber and Morris [25]) to:

$$d\ (C_t\ /\ C_o)\ /\ dt = -\ \beta_L S \qquad\qquad (2)$$

So the external mass transfer rate, $\beta_L S$, is approximated by the initial slope of the $C_t\ /\ C_o$ vs. time graph and can be calculated either by assuming a polynomial relation between C_t/C_0 and time or based on the assumption that the relation-ship was linear for the first initial rapid phase. The first technique was used here.

2- Intraparticle diffusion resistance model

Weber and Morris [25] demonstrated that in intraparticle diffusion studies, rate processes are usually expressed in terms of square root of time. So q_t or fraction metal sorbed is plotted against $t^{0.5}$ as follow:

$$q_t = kt^{0.5} \qquad\qquad (3)$$

where: q_t is the solute concentration in the solid and k the slope of the plot. If particle diffusion is rate controlling, the plots q_t versus $t^{0.5}$ are linear and the slope of the plots is defined as an intraparticle diffusion rate parameter (McKay et al. [23]). In theory, the plot between q_t and $t^{0.5}$ is given by four regions representing the external mass transfer followed by intraparticle diffusion in macro, meso and micropore (Ho and McKay [26]).

MATERIALS AND METHODS

1. Sorbent material and dye

In this work, a waste: orange peel has been employed as a low-cost sorbent material in the removal of acid dyes from synthetic aqueous solutions. It was collected in spring end 2003 from the region of Bensekrane, in Tlemcen-Algeria, in the form of large flakes, cut in small particles of size 1-5 mm and sun/air dried at ambient temperature. It was used as a sorbent material after the following treatment: 10 g of orange peel were contacted with 2 L of distilled water in a beaker agitated vigorously (at a speed of 400 rpm) by a magnetic stirrer at ambient temperature of 25°C during 4 h, then continuously washed with distilled water to remove the surface adhered particles and water soluble materials until constant pH and no colour, and oven-dried at 80°C for 24 h after filtration. This material was crushed and sieved to have particles of size 0.125 – 1.60 mm for further batch sorption experiments.

The dyes used in this study, as commercial salts and whose the structures are unknown, are listed in Table 1. They were kindly donated by SOITEX Company, located in the City of Tlemcen-Algeria. All these dyes were used as received without further purification.

Table 1: List of dyes chosen for the present study

| Commercial name	Colour	Type of dye	λ_{max} (nm)	Supplier
Nylosane Blue	Blue	Acid	591	Sandoz
Erionyl Yellow	Yellow	Acid	407	Ciba-Geigy
Erionyl Red	Red	Acid	522	Ciba-Geigy
Nylomine Red	Red	Acid	510	ICI

Stock solutions (1000 mg/L) of each acid dyes selected were prepared in distilled water. All working solutions of the desired dye concentration were prepared by successive dilutions.
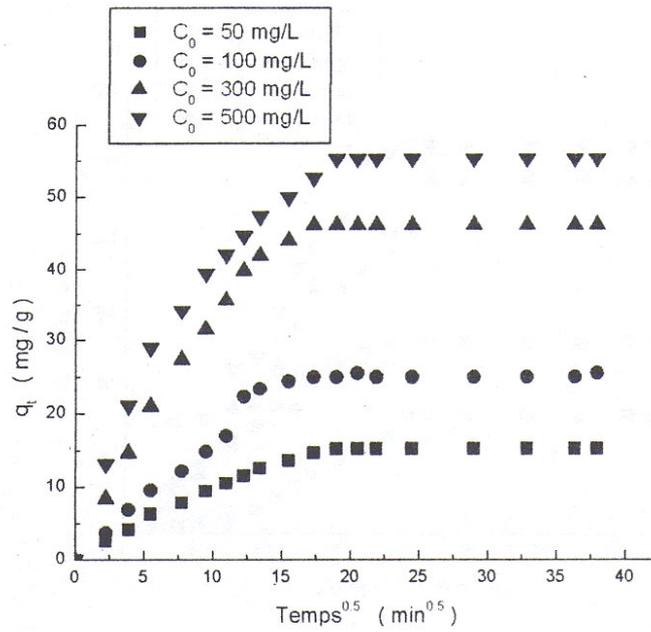
2. Dye sorption kinetics

The experimental systems and procedures have been described elsewhere (Benaïssa [16, 17]).

RESULTS AND DISCUSSION

From a mechanistic viewpoint, to interpret the experimental data, it is necessary to identify the steps involved during dye sorption, described by external mass transfer (boundary layer diffusion) and intraparticle diffusion. Figures 1a, b and c (as a typical example) show plots of C_t / C_o versus time, q_t versus $t^{0.5}$ and Bt versus t for the effect of initial dye concentration on acid dyes sorption by orange peel. Table 2 summarises the mass transfer coefficients for the different kinds of transfer resistance.
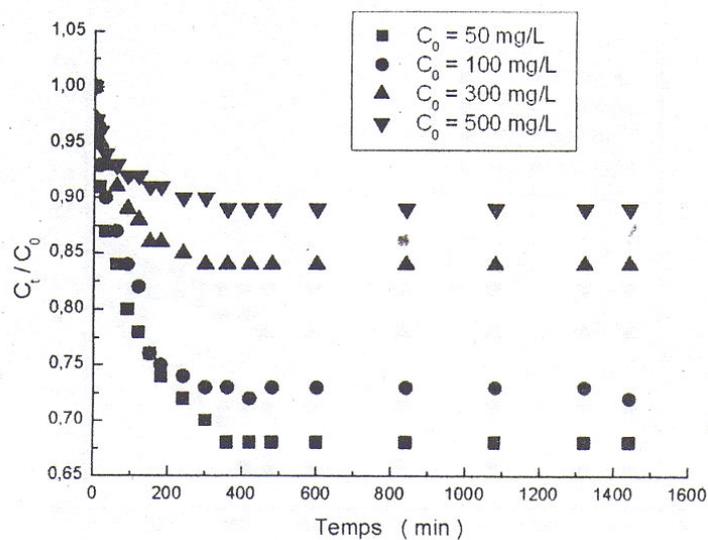
(a)

(b)
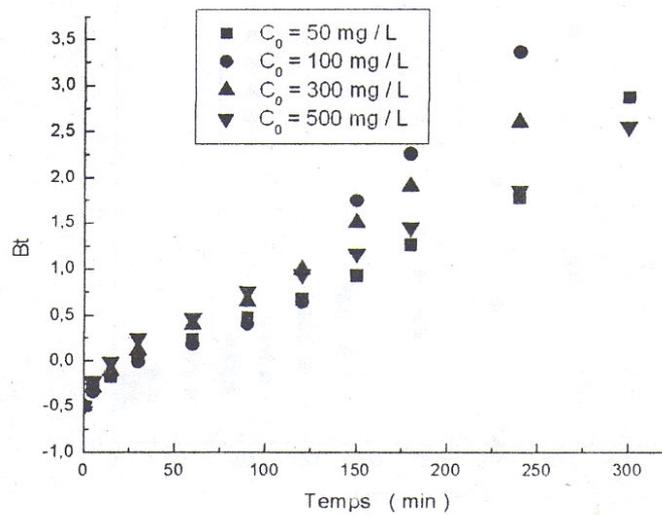
(c)

Figure 1: Effect of initial dye concentration on Nylosane blue sorption kinetics by orange peel (as a typical example): (sorbent dose= 2 g L^{-1}; natural initial solution pH, agitation speed = 400 rpm; particle size = 0.125 – 1.60 mm, T = 25°C) (a) C_t/C_o versus t, (b) q versus $t^{0.5}$ and (c) Bt versus t

Table 2: Effect of initial dye concentration on diffusion coefficients for acid dyes sorption by orange peel. (sorbent dose= 2 g L^{-1}; natural initial solution pH, agitation speed = 400 rpm; particle size = 0.125 – 1.60 mm, T = 25°C)

[dye] (mg/L)	External mass transfer $\beta_L S \times 10^3$ (min^{-1})	Intraparticle diffusion k (mg g^{-1} min$^{-0.5}$)	C (mg/g)	Boyd model B.10^3 (min^{-1})	R^2
Nylosane blue					
50	5.93	0.49	6.12	9.88	0.9782
100	5.90	0.41	17.90	15.19	0.9525
300	3.93	1.20	25.43	12.33	0.9935
500	3.48	1.92	20.10	9.11	0.9792
Erionyl yellow					
50	6.12	0.26	7.34	8.45	0.9869
100	3.83	0.29	16.37	8.75	0.9947
300	2.80	1.11	17.16	6.42	0.9773
500	2.47	1.61	17.78	7.49	0.9747
Erionyl red					
50	6.45	0.33	3.85	12.15	0.9916
100	4.10	0.24	9.95	9.62	0.9947
300	1.42	0.58	12.86	10.64	0.9935
500	1.36	0.87	15.04	8.81	0.9914
Nylomine red					
50	10.70	0.08	13.96	20.18	0.9766
100	5.43	0.21	20.04	12.74	0.9944
300	4.60	0.31	37.72	12.44	0.9944
500	1.88	0.69	38.06	9.47	0.9959

From results obtained from Fig. 1a (as a typical example) and presented in Table 2, the values of mass transfer coefficients obtained for the different kinds of transfer resistance are dependent on both initial dye concentration and the type of dye used. For all acid dyes tested, the external film mass transfer coefficient ($\beta_L S$) decreases as

the initial dye concentration increases. This result is not consistent with the fact external transport can become the rate-limiting step in systems, which have a dilute concentration of solute (Sag and Aktay [18]). In Figure 1b (as a typical example) showing q_t versus $t^{0.5}$, except nylosane red with three linear regions, for all other acid dyes tested two linear regions were observed in the same experiment. McKay et al. [23] explains a non linear plot by a variety of intraparticle diffusion resistance mechanisms, depending on diffusion through pores of various sizes. A first linear portion ended with a smooth curve followed by a second linear portion. The double nature of the curve reflects the two-stage external mass transfer followed by intraparticle diffusion of acid dyes onto orange peel particles. The slope of the second linear portion characterizes the rate parameter corresponding to the intraparticle diffusion, whereas the intercept, C (mg/g), is proportional to the boundary layer thickness: the larger intercept the greater is the boundary layer effect (Kumar et al. [27]). Here, the intraparticle diffusion, k, at different initial dye concentrations, is found from the slope of the second linear region: it increases as initial dye concentration increases. For all acid dyes studied, a positive and significant ordinate intercepts is obtained, indicating the influence of external rate control (Slag and Aktay [18]) which also increases with initial dye concentration. Concerning the type of dye, a possible explanation for the difference in the values of mass transfer coefficients for the different kinds of transfer resistance can be given on the basis of their molecular dimension and structural complexity.

As the double nature of the intraparticle diffusion plot, the sorption process is found to be of a complex nature. Thus in order to characterize what the actual rate-controlling step involved in acid dyes sorption process is, the sorption data were further analysed by the kinetic expression given by Boyd et al. [28].

$$F = 1 - (6/\pi^2) \exp(-Bt) \tag{4}$$

where F is the fraction of solute sorbed at different times t and Bt is a mathematical function of F and given by:

$$F = q_t/q_\infty \tag{5}$$

where, q_t and q_∞ represents the amount sorbed (mg/g) at any time t and at infinite time (in the present study 4-8 h depending on both the initial dye concentration and the type of dye (Benaïssa, [16,17]).

Substituting Eq. (4) into Eq. (5), the kinetic expression becomes:

$$Bt = -0.4967 - \ln(1 - q_t/q_\infty) \tag{6}$$

Thus the value of Bt can be calculated for each value of F using Eq. (6) and plotted against time. The linearity of this plot will provide useful information to distinguish between external transport and intraparticle transport controlled rates of sorption (Kumar et al. [27]). From Fig. 1c (as a typical example), it was observed that the plots

were linear but did not pass through the origin, indicating that, for the all experimental parameters studied here, external mass transport mainly governs the rate-limiting process (Boyd et al. [28]).

CONCLUSION

Analysis of diffusion mechanisms of acid dyes sorption by orange peel was problematic. Diffusion mechanisms were predominant in rate controlling steps. Three models of transfer control were examined: external mass transfer, via a film resistance, the intraparticle diffusion model and Boyd model. These models were not easily applied to evaluate variations in rates and diffusivities. Initial dye concentration has effects on mass transfer coefficients. Under our experimental conditions, the analysis of mechanistic steps involved in acid dyes sorption process confirms that the sorption process is particle-diffusion-controlled, with some predominance of some external mass transfer at the initial stages.

ACKNOWLEDGEMENTS

REFERENCES

[1]   Zollinger H., Color chemistry: synthesis, properties and applications of organic dyes and pigments, 2nd Ed. VCH Publisher, New York, 1991.

[2]   Selvam, K., Swaminathan, K. and Chae, K-S., Bioresource Technology, Vol. 88, pp. 115-119, 2003.

[3]   Fu, Y. and Viraraghavan, T., Fungal decolourization of dye wastewater: a review, Bioresource Technology, Vol. 79 (3), pp. 251-262, 2001.

[4]   Robinson, T., McMullan, G., Marchant, R. and Nigam, P., Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative, Bioresource Technology, Vol. 77, pp. 247-255, 2001.

[5]   O'Mahony, T., Guibal, E. and Tobin, J.M., Reactive dye biosorption by *Rhizopus arrhizus* biomass, Enzyme and Microbiology Technology, Vol. 31, pp. 456-463, 2002.

[6]   Poots, V.J.P., McKay, G. and Healy, J.J., The removal of acid dye from effluent using natural adsorbents-1 Peat, Water Research, Vol.10, pp. 1061-1066, 1976.

[7]   Willmott, N., Guthrie, J. and Nelson, G. The biotechnology approach to colour removal from textile effluent, Journal of the Society of Dyers and Colourists, 114(2), pp. 38-41, 1998.

[8]   Ofomaja, A.E. and Ho, Y-H., Equilibrium sorption of anionic dye from aqueous solution by palm kernel fibre as sorbent, Dyes and Pigments, Vol. 74, pp. 60-66, 2007.

[9]   Garg, V.K., Gupta, R., Yadav, A. B. and Kumar R., Dye removal from aqueous solution by adsorption on treated sawdust, Bioresource Technology, Vol. 89, 121-124, 2003.

[10]   Kapdan, I. K., Kargi, F., Mcmullan, G. and Marchant, R., Biological decolorization of textile dyestuff by *Coriolus versicolor* in a packed column reactor, Environmental Technology, Vol. 21, pp. 231-236, 2000.

[11]   Porter, J. F., McKay, G. and Choy, K. H., The prediction of sorption from a binary mixture of acidic dyes using single-and mixed-isotherm variants of the ideal adsorbed solute theory, Chemical Engineering Science, Vol. 54, pp. 5863-5885, 1999.

[12]   Namasivayam, C., Muniasamy, N., Gayatri, K., Rani, M., Ranganathan K., Removal of dyes from aqueous solutions by cellulosic waste orange peel, Bioresource Technology, Vol. 57, pp. 37-43, 1996.

[13]   Sivaraj, R., Namasivayam, C., Kadirvelu, K., Orange peel as an adsorbent in the removal of acid violet 14 (acid dye) from aqueous solutions, Waste Management, Vol. 21, (2001), pp. 105-110, 2001.

[14]   Annadurai, G., Juang, R-S., Lee, D-J., Use of cellulose-based wastes for adsorption of dyes from aqueous solutions, Journal of Hazardous Materials, Vol. B92, pp. 263-274, 2002.

[15]   Arami, M., Limaee, N.Y., Mahmoudi, N.M., Tabrizi, N.S., Removal of dyes from colored textile wastewater by orange peel adsorbent: equilibrium and kinetic studies, Journal of Colloid and Interface Science, Vol. 288, pp. 371-376, 2005.

[16]   Benaïssa, H., Removal of acid dyes from aqueous solutions using orange peel, Proceedings of 10th International Water Technology Conference (IWTC9 2005), 17-20 March 2005, Sharm Al-Sheikh - Egypt, Vol.3, 1175-1187. Copyright: 2005, Edition 3, ISBN: 977-5069-80-7.

[17]   Benaïssa, H., Removal of acid dyes from aqueous solutions using orange peel as a sorbent material, International Journal of Environment and Pollution, Vol. 34 (1/2/3/4), pp. 71-82, 2008.

[18]   Sag, Y. and Aktay, Y., Mass transfer and equilibrium studies for the sorption of chromium ions onto chitin, Process Biochemistry, Vol. 36, pp. 157-173, 2000.

[19]   Furusawa, T. and Smith, J.M., Fluid-particle and intraparticle mass transport rates in slurries, Industrial Engineering Chemical Fundamental, Vol. 12, pp. 197-203, 1973.

[20]   Findon, A., McKay, G. and Blair, H.S., Transport Studies for the sorption of copper ions by chitosan, Journal of Environment and Science of Health, Vol. 28, pp. 173-185, 1993.

[21]   Tsezos, M. and Volesky, B., The mechanism of uranium biosorption by rhizopus arrhizus, Biotechnology and Bioengineering, Vol. 24, pp. 385-401, 1982.

[22] Peniche-Covas, C., Alvarez L.W. and Arguelles-Mona, W., The adsorption of mercuric ions by chitosan, Journal of Applied Polymer and Science, Vol. 46, pp. 1147-1150, 1992.

[23] McKay, G., Blair, H.S. and Findon, A., Sorption of metal ions by chitosan. In: Heccles, Hunt, S. (Eds.), Immobilization of Ions by Biosorption. Ellis Horwood Ltd., Chichester, pp. 59-69, 1986.

[24] McKay, G. and Poots, V.J.P., Kinetics and diffusion processes in colour removal from effluent using wood as an adsorbent, Journal of Chemical Technology and Biotechnology, Vol. 30, pp. 279-282, 1984.

[25] Weber, W.J. and Morris, G.C., Removal of biologically-resistant pollutants from waste waters by adsorption. In: Advances in Water Pollution Research. Proc. 1st Int. Conf. on Water Pollution Res., Pergamon Press, New York, pp. 231-266, 1962.

[26] Ho, Y.S. and McKay, G., The kinetics of sorption of basic dyes from aqueous solution by sphagnum moss peat, Canadian Journal of Chemical Engineering, Vol. 76, pp.822-827, 1998.

[27] Kumar, K.V., Ramamurthi, V. and Sivanesan, S., Modeling the mechanism involved during the sorption of methylene blue onto fly ash, Journal of Colloid and Interface Science, Vol. 284, pp. 14-21, 2005.

[28] Boyd, G.E., Adamson, A.W. and Myers, L.S., The exchange adsorption of ions from aqueous solutions by organic zeolites. II. Kinetics, Journal of American Chemical Society, Vol. 69 (11), pp. 2836-2848, 1947.